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Towards Greener and More Sustainable Manufacture of Bauxite-Derived Adsorbents for Water Defluoridation

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ABSTRACT

The bauxite-derived adsorbent, activated alumina (AA), has a current annual global market of over 600 million USD, and of this more than one-third of AA is used for defluoridation of fluoride-bearing water. The commonly used Bayer process for production of AA suffers from thermodynamic inefficiency thereby raising costs, and also causes significant environmental damage. Here, we evaluate three other bauxite-derived adsorbents as alternatives to AA for water defluoridation: mildly processed bauxite, thermally activated bauxite, and acid-treated thermally activated bauxite (ATAB). We first determine the energy intensity and resource efficiency of these three new adsorbents throughout their (future, anticipated) manufacturing processes, and compare their defluoridation performance in the laboratory. Then, we quantify the carbon footprints of the three adsorbents via the product life-cycle approach, from their manufacturing to their

applications in defluoridation. The results reveal that these three adsorbents exhibit less energy intensity and higher resource efficiency, thereby lowering their carbon footprints by 2–20X, relative to equivalent amount of AA. We also estimate the operating costs of manufacturing and potential revenues from carbon offsets for each of the three adsorbents. Replacement of about 33,000 tonnes per year of AA currently used for wastewater treatment with equivalent ATAB could annually reduce annual manufacturing costs by 4.7 million USD, and additionally generate 79,200 tonnes CO_2 offsets. This study supports decision-making on selecting a greener and more sustainable approach for wastewater defluoridation.

Keywords: *Activated alumina, The Bayer process, Energy intensity, Resource efficiency, Life cycle, Carbon footprint, Cost-benefit analysis.*

INTRODUCTION

As numerous surveys report, excess fluoride concentrations in groundwater used for drinking pose serious public-health threat in many regions, including India,[1] China,[2] Pakistan,[3] several African countries,[4] and even in the US.[5] Currently, more than 100 million people around the world drink groundwater with concentrations above the Maximum Contaminant Limit for F- recommended by the World Health Organization (WHO).[6] Natural processes lead to leaching of fluoride from fluoride-bearing minerals in the rocks and soils into aquifers. Fluoride also enters water via various anthropogenic sources, such as effluent from semiconductor, ceramic, glass and metal-processing industries[7] and atmospheric deposition of fluoride-containing emissions from coal-fired power plants.[8]

Excessive long-term fluoride intake from drinking water is known to cause serious health problems, including dental / skeletal fluorosis,[9] interference with oocyte maturation,[10] and impacts on human thyroid hormones.[11]

Effective fluoride-removal methods can be broadly categorized into two groups: (i) membrane separation and (ii) adsorption. Membrane separation, such as reverse osmosis, is typically high capital costs and energy-intensive (high operation costs), as well as being subject to chemical and biological fouling of membranes (high maintenance costs).[1, 12] Conversely, adsorption appears to be attractive for fluoride removal due to its operational simplicity, cost-effectiveness, and potentially zero-liquid discharge performance, a desired outcome of industrial water treatment technologies.[13] Activated alumina (AA) is a bauxite-derived adsorbent and shows high affinity for fluoride. AA filters are identified by U.S. Environmental Protection Agency (USEPA) as the best technology generally available for water defluoridation.[14] Due to their simplicity of use, technical efficiency and affordability, AA filters have been widely used as an effective adsorptive media for defluoridation of drinking water at community and household levels since the 1940s in industrial countries.

Large quantities of AA are used for defluoridation in water treatment, and the production of AA has significantly grown partly driven by the demand in industrial wastewater treatment market.[15] In 2015, the global AA market was estimated at 95,300 tonnes,[16] where the water treatment industry had a share of ~35% (i.e., ~33,000 tonnes).[17] According to various analyst reports,[16-18] the global market for AA is expected to expand at a compound annual growth rate of 5–8%. In 2017, the worldwide AA market exceeded 620 million USD,[18] and the sales of AA are expected to reach between 0.8 and 1.3 billion USD by 2025.[18, 19] Globally, over 95% of manufactured alumina (Al_2O_3) is obtained from

bauxite ores through the Bayer process.[20] In 2017, ~130 million tonnes of alumina was produced worldwide.[21] Some of this metallurgic-grade alumina is then thermally activated to produce the commonly used AA in filter media. Bauxite ore is readily available around the world, and contains aluminum oxide between 30% and 65% by mass, in three principal aluminum-bearing mineral forms: gibbsite ($Al(OH)_3$ or $AlO(OH)\cdot H_2O$), böehmite (γ-AlO(OH)) and diaspore (α-AlO(OH)). In 2017, the world bauxite production was estimated to be 300 million tonnes (9.1% increase over 2016),[21] of this, around 85% of bauxite is refined into alumina or alumina chemicals.[22] Most of this refined bauxite ends up for metallurgical use as input into aluminum production, and a small fraction goes into manufacture of AA.

The Bayer process for high-grade alumina production was first developed and patented at the end of the 19th century by Karl Joseph Bayer. Since then, successive improvements have increased its engineering performance. The Bayer process generally encompasses a series of complex unit processes (**Table S1** in the Supporting Information), including bauxite milling (to a size of <1.5 mm),[23] digestion (with concentrated caustic soda at 135–245 ^{o}C under a high pressure),[24, 25] clarification (separation of solid impurities from the clear liquor), precipitation (seeded with pure alumina crystals), and activation of the alumina to produce AA by calcination (to 1010–1260 ^{o}C).[23] Details of technological data and specification for the Bayer process are provided in the Supporting Information. Its thermodynamic efficiency remains low (exergy efficiency ~2.9%).[26] The digestion and calcination steps under high temperatures and pressures are energy-intensive, thereby resulting in substantial CO_2 emissions. Another significant environmental burden from the Bayer processes is the safe disposal of red mud (process byproduct); 0.3–2.5 tonnes of red

mud are produced for every tonne of alumina produced.[20] Due to growing alumina demand, the annual energy consumed and resulting greenhouse gas (GHG) emissions for alumina production are expected to increase for the next couple of decades.[27]

Recently, three new bauxite-derived adsorbents, i.e., mildly processed bauxite (MPB), thermally activated bauxite (TAB) and acid-treated thermally activated bauxite (ATAB), have been developed for providing economically viable and environmentally friendly adsorbents that can be used in wastewater treatment. For ease of intercomparison of the three new adsorbents and AA, we use the concept of maximum adsorption density, which refers to the maximum possible amount of adsorbate that can be captured on an adsorbent (i.e., when in equilibrium with a saturated solution). We note first that this parameter is dependent on the adsorption isotherm behavior. In the case of MPB and TAB, isotherms follow Freundlich, while ATAB and AA isotherms exhibit Langmuir-Linear behavior. Second, the parameter is only tangentially related to the actual amount of adsorbent needed to reduce a specific initial high concentration to a specific final desired low concentration. Cherukumilli et al.[28] first developed a two-step process to produce the MPB for water defluoridation. They obtained MPB adsorbent with a calculated maximum fluoride adsorption density of 2.29 mg/g, based on adsorption isotherm studies. Subsequently, Cherukumilli et al.[29] used a thermal activation process to produce TAB and improved the maximum fluoride adsorption density to 3.82 mg/g. Haddad et al.[30] introduced another approach to manufacturing bauxite-based adsorbents through an ATAB process. ATAB exhibits an even higher maximum fluoride adsorption density of 7.47 mg/g, approaching that of commercially made AA, ~8.40 mg/g.[31] The ATAB materials also have a large BET surface area of ~400 m^2/g, which is higher compared with commercial AA (e.g., ~200

m^2/g)[32] available in the market, as well as MPB (e.g., ~17 m^2/g)[28] and TAB (e.g., ~170 m^2/g).[29]

To the best of our knowledge, little-to-no published research exists assessing the life-cycle of manufacturing processes for different bauxite-derived adsorbents that could replace AA. Current literature on life-cycle assessment is limited only to the Bayer refining and Hall-Héroult smelting process.[33] This article provides an insight into the implementation of green chemistry principles in water defluoridation by comparing different types of bauxite-derived adsorbents from the perspective of their environmental performance. We compare four types of bauxite-derived adsorbents, i.e., (1) commercial AA from the Bayer process, (2) MPB adsorbents, (3) TAB adsorbents and, (4) ATAB adsorbents. We first evaluate the energy intensity and resource efficiency of manufacturing processes for these four different bauxite-derived adsorbents. Then, we determine their carbon footprint throughout the product life-cycle from adsorbent manufacturing to applications for groundwater defluoridation. We also perform a preliminary cost benefit analysis for different scenarios of bauxite-derived adsorbents by considering the manufacturing costs and carbon credits from CO_2 emissions avoidance throughout the product life-cycle.

METHODS

Scenario Set-up for Bauxite-derived Adsorbents

We set up scenarios for four major processes to manufacture bauxite-derived adsorbents, i.e., commercial AA produced from the Bayer process (denoted as Bayer), the MPB process (denoted as MPB), the TAB process (denoted as TAB), and the ATAB

process (denoted as ATAB), as shown in **Table 1**. In Bayer, the bauxite-derived AA is manufactured through the Bayer process, including milling, caustic digestion, clarification, precipitation and calcination. The inventory data and details of each unit process in Bayer were gathered from the literature[26, 28] and are summarized in the Supporting Information. In the milling process, the as-received bauxites are ground from an initial particle size ranging from 0.1–3.0 cm to a final size around 1 μm. The energy consumptions of the milling, caustic digestion, and calcination processes were as measured directly by various authors, and we obtained these from the published literature,[26, 28] while the energy requirements of clarification and heating for precipitation at 60 ^{o}C were extracted from the ecoinvent database (version 3.2). In MPB, the ground bauxite is first dried at 100 ^{o}C for 1 h, and then milled. In TAB, the ground bauxite is dried and milled, and then thermally activated by heating to 300 ^{o}C for 4 h. In ATAB, the ground bauxite is first dried and milled, then thermally activated at 300 ^{o}C, and then is treated with 5 M HCl at room temperature.

Table 1. Descriptions and specification of different scenarios for manufacturing bauxite-derived adsorbents.

Adsorbent synthesis [c]	Manufacturing conditions	Combinatorial treatment	Notation	Ref.
The Bayer process	Digested with NaOH at 140–300 ^{o}C and 3.5 MPa, precipitated at 60 ^{o}C and then calcined at 1100 ^{o}C	None	Bayer	[26, 28]
The MPB process	Dried at 100 ^{o}C for 1 hr and then milled	None	MPB	[28]
The TAB process	Dried at 100 ^{o}C for 1 hr, milled and then heat activation at 300 ^{o}C for 4 hr	None	TAB	[29]
The TAB process	Dried at 100 ^{o}C for 1 hr, milled and then heat activation at 300 ^{o}C for 4 hr	Acidification by 1.1 M HCl to maintain pH at 6.0	TAB-HCl	[29]
The TAB process	Dried at 100 ^{o}C for 1 hr, milled and then heat activation at 300 ^{o}C for 4 hr	Acidification by pressurized CO_2 to maintain pH at 6.0	TAB-CO_2	[29]
The ATAB process	Dried at 100 ^{o}C for 1 hr, milled, heat activation at 300 ^{o}C for 4 hr, and then followed by 5 M HCl treatment	None	ATAB	[30]

Note: Basic data for each scenario is summarized in the Supporting Information.

Research has shown that treatment of groundwater to lower its pH, such as mild acidification to a pH of 6.0 ± 0.1,[29] can effectively improve fluoride adsorption, and thus reduce the required dose of adsorbents. Therefore, we also explore here the effect of mild acidification of groundwater for defluoridation with TAB, including acidification of groundwater by HCl (denoted as TAB-HCl), and acidification by pressurized CO_2 (denoted as TAB-CO_2). The specification and process data of each scenario are provided in the Supporting Information.

Process Energy Intensity and Resource Efficiency

To identify the best available method for producing bauxite-derived adsorbents, we determined both the energy intensity and resource efficiency of four major scenarios of manufacturing processes (i.e., Bayer, MPB, TAB and ATAB). The process energy intensity of each scenario for manufacturing one kilogram of adsorbent (kWh/kg) was determined by compiling the reported experimental data in the literature. The energy consumption of main unit processes, such as bauxite milling, dried, digestion, calcination, thermal activation and acid treatment, were included.

The mass resource efficiency of each scenario was evaluated using the concept of *E* factor, representing the total mass of wastes produced throughout the processes per unit mass yield of the final product. The *E* factor considers, in mass terms, both the product yield and wastes from all of the auxiliary components, such as chemicals used in work-up and solvent losses. The *E* factor provides a useful metric for assessing most industrial processes (an exemplar exception would be thermal power generation). Sheldon et al.[34] offer a definition of waste as "everything but the desired product." For manufacturing of bauxite-derived adsorbents, the major sources of waste are the reacted solution (e.g., waste caustic or acid) and solid wastes (e.g., red mud from the Bayer process). Therefore, in this study, we define the *E* factor as eq (1):

$$E\ \text{factor} = \frac{m_{\text{bauxite}} + \sum m_{\text{reagents}} + m_{\text{water}} - m_{\text{product}}}{m_{\text{product}}} \quad (1)$$

The *E* factors are determined on a gate-to-gate basis, i.e., from the input of bauxite feedstock (factory's receiving gate) to the final adsorbent product (factory's shipping gate),

and include only those processes conducted at the manufacturing site of adsorbents. A higher *E* factor represents more waste generated (by mass) during the processes, and is usually well correlated with higher manufacturing costs for waste treatment or disposal. The ideal *E* factor of a process should be zero, indicating a scenario of zero waste generation. Note that the *E* factor does not incorporate embodied wastes in the inputs (e.g., in the manufacture of reagents, or coal ash or CO_2 generated in production of electricity).

Carbon Footprint Analysis: Scope of Work, Definition and Functional Unit

The carbon footprints of different manufacturing processes for bauxite-derived adsorbents were determined through the product life-cycle approach using the Umberto software (version 5.6, Ifu Hamburg, Germany). The carbon footprint analysis follows the standard procedures of life cycle assessment described in the ISO 14040[35] and 14044.[36] For the product life-cycle approach, the main manufacturing processes and their associated environmental flows (i.e., inputs from the environment without prior human transformation and outputs to the environment without further human transformation)[37] should be considered. In this study, the system boundary (Figure 1) incorporates bauxite milling through different manufacturing steps prior to the final adsorbent products, consisting of all inputs (e.g., chemicals, electricity and auxiliary agents) and outputs (e.g., adsorbent products, waste heat, air pollutant emissions, wastewater and solid wastes). We did not consider bauxite mining, feedstock transport, and final waste disposal, such as red mud and waste acids, in the carbon footprint analysis. It is noted that the waste disposal is primarily covered by the exclusive waste-management-related service.[38] We also did not evaluate the carbon footprint due to the regeneration of saturated adsorbents after defluoridation.

Although the saturated adsorbents can be regenerated, for simplicity of analysis, we applied these methods assuming only one-time use of all four adsorbents. In practice,[15] the regeneration involves a two-step or a one-step process using 1% NaOH to raise the pH of column to 13.0 for 100 min.

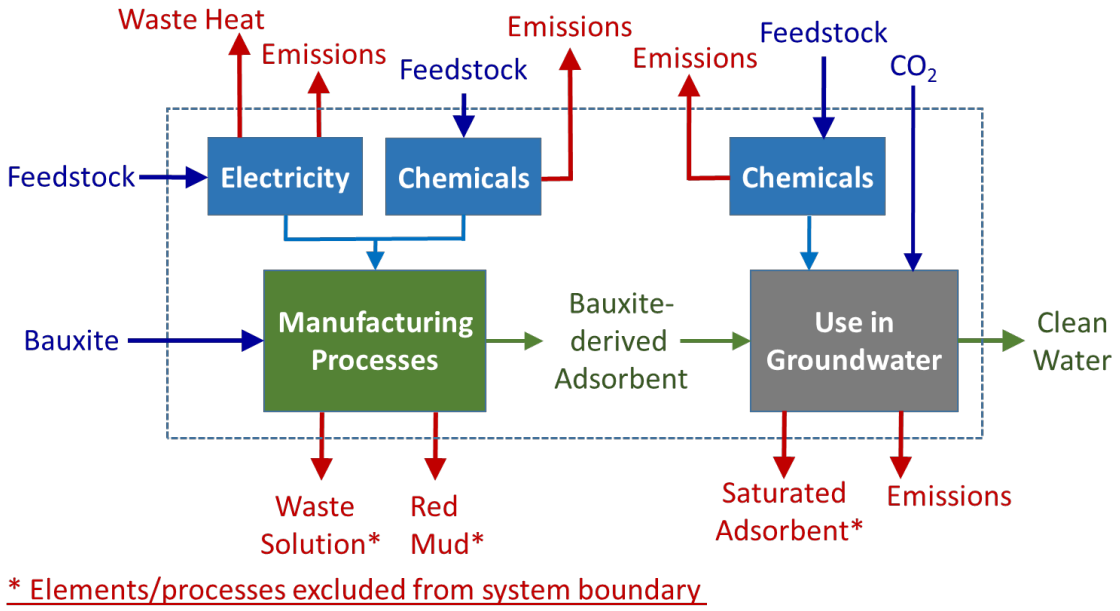

Figure 1. System boundary of product life-cycle analysis for bauxite-derived adsorbents used in groundwater defluoridation, defined by the functional unit of the specific dose of adsorbents needed to remediate contaminated groundwater (10.0 mg-F^-/L) to the WHO-MCL (1.5 mg-F^-/L).

The functional unit of carbon footprint analysis is designated to be a "service", i.e., the specific dose of adsorbents (D_s, kg of adsorbent per tonne of contaminated groundwater) needed to remediate contaminated groundwater (i.e., 10 mg F- per liter) to the WHO's Maximum Contaminant Limit (MCL = 1.5 mg F^- per liter). The value of D_s for each scenario was experimentally determined with batch tests using incremental adsorbent doses on a gram per liter basis,[28-30] i.e., how many grams of adsorbent is needed to remediate 10 ppm F^- contaminated water to under 1.5 ppm F^-. Analysis using these values in this

manuscript has been converted to units of kg of absorbent needed per tonne of groundwater treated for purposes of effectively assessing adsorbent use on industrial scales.

The carbon footprint of the manufacturing processes was expressed as kg CO_2-equiv per functional unit based on ReCiPe midpoint impact assessment.[39] Resting on the work of the Intergovernmental Panel on Climate Change (IPCC), carbon footprint analysis applies a life-cycle perspective and inventories the six GHGs stated in the Kyoto Protocol. For instance, all CO_2, CH_4 and N_2O emissions were summed using global warming potentials of 1, 30, and 265 CO_2-equiv, respectively, from the IPCC,[40] representing equivalences for a time horizon of 100 years. The manufacturing data for all chemicals (e.g., hydrochloride, sodium hydroxide and lime) and electric power generation in the US were obtained from secondary sources in the ecoinvent database (version 3.2) in the Umberto.

The carbon footprint (*CF*) of manufacturing processes can be defined as eq (2):

$$CF = CF_{dir} + CF_{ind,che} + CF_{ind,wat} \quad (2)$$

Following the system boundaries illustrated in **Figures S1-S4** (see the Supporting Information), the carbon footprints of different adsorbents manufacturing processes, including GHG emissions from energy use (CF_{dir}), chemicals manufacturing ($CF_{ind,che}$), and water production ($CF_{ind,\ water}$), were determined.

Preliminary Cost-Benefit Analysis

The economically rational agent in the supply chain normally selects the material supplier offering the lowest price regardless of the green factor. To effectively promote the

use of the greener alternative (lower carbon footprint) in wastewater treatment plants, the price of the alternative products should be competitive to that of the commonly used AA, while providing additional revenues from carbon offsets. In this study, a preliminary analysis of operating costs of different processes for manufacturing bauxite-derived adsorbents is performed. The initial capital investment in factories and equipment is therefore not considered. Our analyses also do not include potential adsorbent losses during defluoridation, or the costs of adsorbent regeneration and disposal of resulting waste. For different scenarios, we estimated their operating costs for manufacturing, and revenues obtained from any CO_2 offsets (using AA as the baseline) based on remediating one tonne of impaired water. The operating costs for manufacturing (OC_{manu}) based on the required minimal dose of adsorbents to achieve the WHO-MCL requirement were determined by eq (3):

$$OC_{manu} = C_{bau} + C_{che} + C_{ele} \quad (3)$$

where C_{bau}, C_{che} and C_{ele} were the costs of raw bauxite, chemicals used in processes, and electricity, respectively. The material cost of crude-dry bauxite is assumed to be 0.03 USD/kg according to current market prices.[21] For the chemicals used in processes, the average prices of limestone, sodium hydroxide and hydrochloric acid were 0.01, 0.30 and 0.25 USD/kg, respectively, and the specifications of each chemical can be found in **Table S6** (see the Supporting Information). The average electricity tariff for industrial uses in the USA in 2016 was 0.0676 USD/kWh.[41]

For carbon credits, the revenues of CO_2 offsets (R_{CO_2}) were calculated by eq (4), where the carbon footprint of the Bayer-AA (CF_{AA}) served as the baseline.

$$R_{CO_2} = (CF_{AA} - CF_{alt}) \times P_{CO_2} \quad (4)$$

where CF_{alt} was the carbon footprint of alternative adsorbents, viz. MPB, TAB, and ATAB. P_{CO_2} was the market price of carbon offsets. It should be noted that the voluntary offsets of carbon emission reductions operate within a different market, where buyers may pay differently for the same amount of carbon offsets. In our economic evaluation, we used the average California marketplace price for carbon offsets sold in 2018, which was about USD 15.00 per tonne of CO_2 equivalent (t-CO_2e).[42]

RESULTS AND DISCUSSION

Energy Intensity and Resource Efficiency for Adsorbent Manufacturing Processes

Although widely deployed for manufacturing bauxite-derived adsorbents, and having been improved over several past decades, the Bayer process for production of AA is still considered as an energy- and resource-intensive method and significant concerns arise from the environmental pollution from its use.[33] To identify a potential alternative, we first examine the energy intensity and resource efficiency of different adsorbent manufacturing processes. Figure 2 shows the process energy intensity (EI, units of kWh/kg of adsorbent) for adsorbent manufacturing and the fluoride adsorption density (C_{ad}, units of mg/g) in groundwater for each adsorbent. The EI values of AA, MPB, TAB and ATAB were 4.95, 0.36, 0.43 and 0.56 kWh per kg of adsorbent. The Bayer process for production of AA was the most energy-intensive method, where digestion and calcination accounted for 54% and 23% in the total EI, respectively. However, the fluoride adsorption density of AA was also the highest (i.e., 8.40 mg/g) among four scenarios. Similarly, in MPB, although the EI of manufacturing processes was the lowest, the adsorption density was also the lowest (i.e.,

2.29 mg/g). This would result in a larger amount of spent adsorbent generated with MPB, compared to AA, to achieve the same defluoridation performance of groundwater. In contrast, the EI and adsorption density in ATAB were found to be well balanced. In the case of ATAB, the EI was 88.7% lower than that in AA; however, 88.9% of the adsorption density in AA could be retained (i.e., 7.47 mg/g).

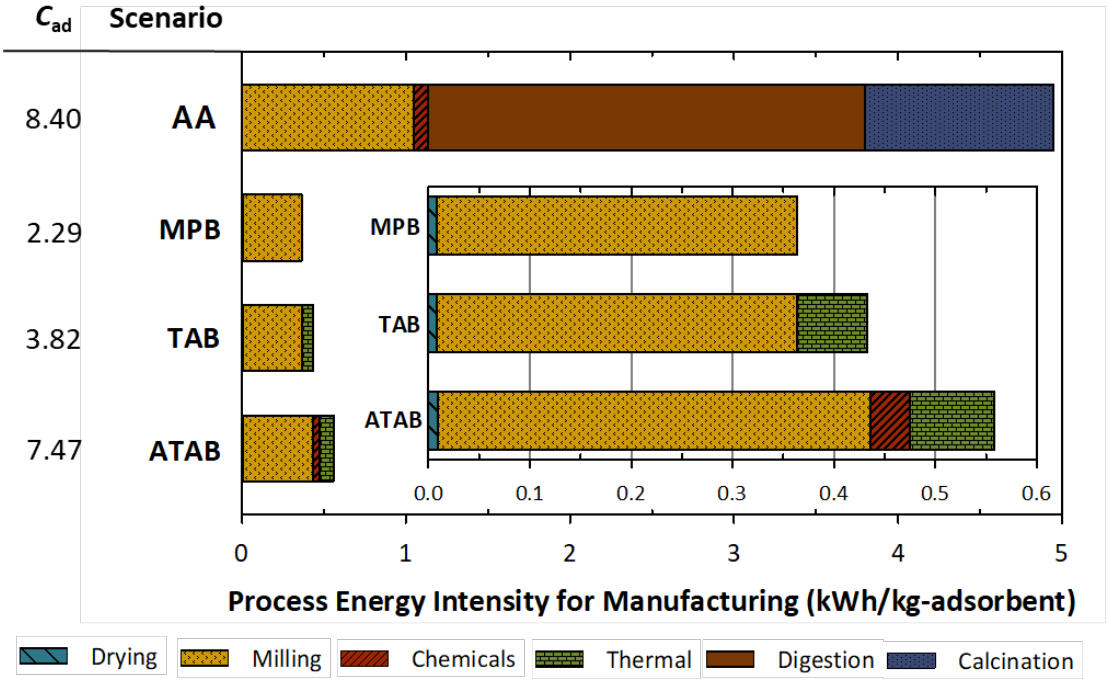

Figure 2. Process energy intensity (*EI*, kWh/kg of adsorbent) for adsorbent manufacturing, including AA (activated alumina from the Bayer process), MPB (mildly processed bauxite), TAB (thermally activated bauxite) and ATAB (acid-treated thermally activated bauxite). Inset in the Figure is magnified for clarity to show the contributors to the EI of the three new adsorbents. Note that C_{ad} (mg/g) shown in the left column is the earlier discussed metric, called maximum adsorption density, for fluoride of each adsorbent.

For the mass resource efficiency, we considered the actual amount of wastes generated throughout the manufacturing processes by determining the *E* factor of each scenario (see definitions in eq (1)). In this study, the inventory data, such as bauxite, reagent, solid waste, wastewater and product, for AA, MPB, TAB and ATAB were gathered from the

literature,[15, 26, 31, 32] where the quantities of process inputs and outputs were experimental determined. As presented in Table 2, the *E* factors of AA, MPB, TAB and ATAB were found to be 7.73, 0.01, 0.18, and 0.27, respectively, indicating that the Bayer process for production of AA exhibited the lowest mass resource efficiency among the four scenarios. In the Bayer process, between 0.7 and 2.0 tonnes (dry weight) of red mud are produced (in the extremes, the red mud production ranges from 0.3 to 2.5 tonnes) for every tonne of alumina produced.[20] Research has shown that the alumina industry (based on the Bayer process) produces around 120 million tonnes of red mud per annum,[43] and the total accumulative red mud produced worldwide has been estimated to about 3 billion tonnes.[44] Currently, the recycled fraction of red mud is relatively small, and most of the red mud is regularly stored in huge tailing ponds close to the facility with proper permits. These tailing ponds carry great risks and have on occasion resulted in loss of human lives and environmental catastrophes, such as accidental large scale contamination of aquifers and soil, and toxicity to plant and animal life.[45]

The amount of water use in AA was also intensive (a share of ~69% in the total weight of input materials), while the loss of steam throughout the processes was relatively small (< 7% in the total weight of outputs). This implies that the Bayer process would generate a great amount of wastewater that needs to be carefully treated prior to discharge. In contrast, these three alternatives (MPB, TAB and ATAB) do not generate a substantial quantity of wastewater during manufacturing, thereby approaching the goal of zero-liquid discharge as well as reducing reliance of external water sources in industrial processes.[13] For the ATAB, a nominal amount of a side stream of HCl solution (~6% in the total weight

of outputs) is generated, which could be potentially recycled and reused after the acid activation stage.

Similar to the aforementioned findings of energy intensity, while the *E* factor of manufacturing processes in MPB and TAB is quite low (0.01 and 0.18, respectively), the maximum adsorption density of the obtained adsorbents is roughly 2–3 times lower than that for AA made from Bayer, thereby requiring a greater dose of adsorbents (see the D_s value in Table 1). After use in defluoridation treatment, MPB and TAB would generate comparable amounts of spent adsorbent, which is not revealed in the value of the *E* factor. In contrast, while ATAB also exhibits a significantly lower *E* factor (i.e., 0.27) than that of AA, it demonstrates a maximum adsorption density comparable to AA for subsequent applications in defluoridation. Moreover, the minimum adsorbent dose (D_s) for ATAB (1.5 kg of adsorbent for remediating a tonne of groundwater) is significantly less than that of AA (4.0 kg/tonne). Therefore, despite generating a small amount of HCl waste during the manufacturing, ATAB was evaluated as a greener manufacturing method in comparison to the Bayer process for AA. It is noteworthy that the maximum adsorption density (C_{ad}) in Table 2 reflects the maximum possible amount of fluoride that can be captured on an adsorbent at equilibrium with a saturated solution. In practice, the D_s value is used as the basis for the subsequent analysis and intercomparison of the adsorption performance at field operations (where equilibrium is usually not reached). The D_s value is determined by experiments that remediating a tonne of groundwater from 10 mg F^-/L to below the WHO's MCL (1.5 mg F^-/L).

Table 2. Resource efficiency for each manufacturing scenario. Characterization and groundwater defluoridation performance of four types of bauxite-derived adsorbents. Assumed that the bauxite was collected from a mine in India.

Manufacturing [a]									Characteristic of adsorbents [c]				Ref.
Process	Input bauxite (kg)	Input reagents (kg)	Input water (kg)	Output product (kg)	Solid waste (kg)	Waste water (kg)	Loss (steam, CO_2) (kg)	*E* factor (-)	D_p (μm)	SSA (m^2/g)	C_{ad} (mg/g)	D_s (kg/tonne)	
Bayer AA	2.65	0.08	6.00	1.00	1.04	6.00	0.54	7.73	0.58 ± 0.56	200	8.40	4.0	[15, 26, 31, 32]
MPB	1.00	-	-	0.99	0.0	-	0.01	0.01	0.71 ± 0.10	17.2 ± 1.4	2.29	22.8 ± 1.0	[28]
TAB	1.00	-	-	0.85	-	-	0.15	0.18	1.08 ± 0.45	169.2 ± 13.2	3.82	10.5–21.3	[29]
ATAB	1.20	0.07	-	1.00	0.20	0.07	-	0.27	0.50 ± 0.78	401 ± 6	7.47 [b]	1.5	[30]

[a] MPB: mildly processed bauxite; TAB: thermally activated bauxite; ATAB: acid-treated thermally activated bauxite.

[b] 10 ppm fluoride-bearing water at pH 6.

[c] D_p: average particle size of adsorbent (μm); SSA: specific surface area of adsorbent (m^2/g); C_{ad}: fluoride adsorption density determined by adsorption isotherms at equilibrium; D_s: minimum adsorbent dose (kg/tonne) required to remediate 10 mg F^-/L to below the WHO's MCL (1.5 mg F^-/L), determined by experiments. The values for these characteristics of adsorbents were gathered from the literature.[15, 28-32]

Carbon Footprint of Adsorbents from Manufacturing to Defluoridation

Although the carbon footprints of adsorbents are largely dependent on the energy intensity of manufacturing processes, the carbon footprints should be evaluated via the product life-cycle approach from adsorbents manufacturing to applications in groundwater defluoridation (see boundary in Figure 1). This provides a fair basis for evaluation by considering the effect of energy consumption in the manufacturing stage and the actual dose required in the defluoridation stage on the carbon footprint for a "service". As mentioned earlier, the "service" in the following analysis is remediating, by adsorption, one tonne of fluoride-contaminated groundwater from an initial concentration of 10 mg/L (as F^-) to a final concentration of 1.5 mg/L (as F^-). Here, the actual doses required for a service in the cases of AA, MPB, TAB and ATAB are 4.0, 22.8, 21.3 and 1.5 kg/tonne, respectively (as shown in Table 2).

Figure 3 shows the carbon footprints of the adsorbents resulting from their production and their use to deliver the above "unit of service" of groundwater defluoridation. For remediating one tonne of groundwater, the carbon footprint of AA produced with the Bayer process was about 10.0 kg CO_2-eq per unit of service. The CO_2-eq emissions of the Bayer process are mainly from the use of fossil-fuel based energy. Contributions of key processes to the total carbon footprint in the Bayer process were identified to be (1) digestion under high temperature and pressure (55%), (2) calcination under high temperature (24%), and (3) feedstock bauxite milling (22%). Embodied CO_2-eq footprints of electrical energy, and chemicals used in production or actual defluoridation process, are included in the footprints of all adsorbents. In contrast, due to the relatively low operating pressure and temperature,

the carbon footprints in MPB, TAB and ATAB were found to be significantly smaller. To achieve the same removal of fluoride in groundwater, these novel low-temperature manufacturing processes (i.e., MPB, TAB and ATAB) could effectively lower the carbon footprints by 53−96%, compared to the Bayer process (for producing AA). In particular, the carbon footprint of ATAB was only 0.4 kg CO_2-eq per service, a huge reduction of ~96% from that of AA. In the case of ATAB, the milling process of bauxite ores was the major contributor (~77% share) to its total CO_2 emissions.

In addition, as noted, mild acidification of groundwater, e.g., by HCl or CO_2, can reduce the needed dose of adsorbents, thus further lowering the carbon footprint throughout the product life-cycle. Here, we evaluate the effect of acidification of groundwater on the carbon footprints of the TAB adsorbents. The actual doses required for a "service" in the cases of TAB with HCl acidification (denoted as TAB-HCl) and TAB with CO_2 acidification (denoted as TAB-CO_2) are 10.5 and 13.6 kg/tonne, respectively. According to the carbon footprint analysis (see Figure 3), in the case of TAB, the original carbon footprint (4.7 kg CO_2-eq per service) can be reduced to 2.3–3.0 kg CO_2-eq per service, if mild acidification of groundwater is deployed prior to defluoridation by adsorption. Thus, mild acidification of groundwater could effectively lower the carbon footprints by 36−51%, compared to that without acidification.

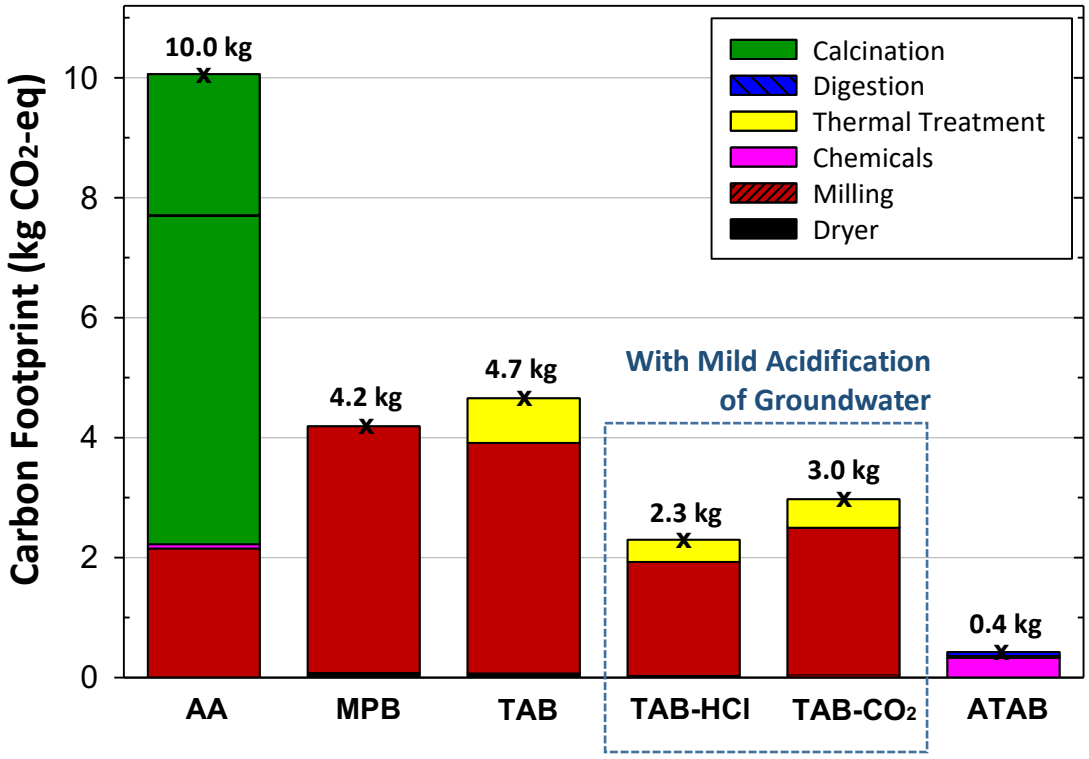

Figure 3. Carbon footprints of four different types of bauxite-derived adsorbents, viz. AA (activated alumina from the Bayer process), MPB (mildly processed bauxite), TAB (thermally activated bauxite) and ATAB (acid-treated thermally activated bauxite), for delivering the same "unit defluoridation service" (defined in the text). The TAB-HCl and TAB-CO_2 are used to evaluate the effect of acidification of groundwater with HCl and CO_2, respectively. Note that the impacts of bauxite mining and waste treatment were not included. The data for the Bayer process was gathered from the ref.[26], where the digestion step in Bayer processes was assumed to be operated at 140–300 ^{o}C and 3.5 MPa, while the calcination was at 1100 ^{o}C. The process data for MPB, TAB is gathered from refs.[28, 29] and ATAB processes is from ref.[30]

The actual values of carbon footprints are sensitive to the generation mix of input electricity. However, regardless of energy source, adsorbents manufactured in the ATAB process achieve the lowest carbon footprint among four major scenarios considered in this study. Thus, alternative adsorbents such as ATAB may be more attractive than AA due to their reduced GHG emissions over the product's life-cycle. The results imply a great

potential of improving the carbon intensity of alumina-based adsorbent manufacturing for wastewater treatment (such as fluoride removal).

Preliminary Cost and Benefit Analyses for Selecting a Green Supplier

In this section, we report results from a preliminary cost-benefit analysis (Figure 4) to provide relevant information for agents in wastewater treatment plants to select greener defluoridation adsorbents that exhibit higher green factors while having lower operating costs for manufacturing. Similar to carbon footprint analysis, the economic analysis herein is performed based on a "service", i.e., the actual dose of adsorbents for remediating one tonne of groundwater by adsorption from 10 to 1.5 mg-F^-/L. For the operating costs of bauxite-derived adsorbents manufacturing (Figure 4(a)), we consider the costs of raw bauxite, electricity and chemicals uses in processes, based on the required minimal dose of adsorbents. The results indicated that both MPB and TAB exhibited lower operating costs for manufacturing, as these processes do not either require extensive use of chemicals or operate under high temperature and pressure. In contrast, both AA from the Bayer process (hereafter abbreviated as "Bayer-AA") and ATAB required a higher cost for chemicals, such as NaOH or HCl, to activate the adsorbents. Among four scenarios, the electricity cost for the Bayer process was the highest since it was typically operated under high temperature and pressure. The results were consistent to the findings illustrated in the section 3.1. If the AA used in wastewater treatment plants was replaced with MPB, TAB and ATAB, the operating costs of manufacturing for adsorbents could be reduced by 35.7, 37.0 and 4.7 million USD per year, respectively (based on the 2015 annual demand of AA for water treatment, namely ~33,000 tonnes). We note that while savings from switching

to MPB and TAB are much larger than those from switching to ATAB, the latter may have a practical advantage from requiring transport, handling and storage of almost 10-times smaller mass for the same service compared to that for MPB and TAB (see Table 2, column titled D_s). More details are discussed below.

Aside from the operating costs for manufacturing, potential revenues from deploying greener processes should be estimated to reveal the benefits of alternatives. This provides the opportunity for additional earning while preserving savings. For instance, if we assumed the total CO_2 emissions in the Bayer process as the baseline, additional economic revenues from carbon offsets in MPB, TAB and ATAB could be earned due to their lower consumption of energy throughout the manufacturing processes. The total revenues of carbon offset in MPB, TAB and ATAB were found to be 0.09, 0.11 and 0.15 USD/service, respectively, as shown in Figure 4(b). The ATAB exhibited the highest revenues of carbon offsets among all scenarios of alternatives. Note that the D_s for the AA from the Bayer process was 4.0 kg for remediating one tonne of impaired water (per "unit of service" defined earlier), as shown in Table 2. For this analysis, we assumed that AA used in wastewater treatment (~33,000 tonnes/year) was replaced by MPB, TAB and ATAB, the total revenues of carbon offsets were expected to be 0.7, 0.9 and 1.2 million USD per year, respectively. One should notice that here we used the average California marketplace of carbon offsets sold in 2018 for the economic evaluation (e.g., ~15.00 USD/t-CO_2e).[42] However, the marketplace of carbon offsets is highly variable and quite different among different countries, locations, times and other attributes. For instance, the price of carbon offset was as high as ~50 USD/t-CO_2e in 2016,[46] and even over 70 USD/t-CO_2e in the first quarter of 2018.[47] This would result in the uncertainty of the economic analysis, and, in

fact, potentially magnify the economic feasibility of these greener adsorbents in some regions as the total revenues of carbon offsets can substantially increase.

While their operating costs for manufacturing are relatively higher, the maximum adsorption densities for fluoride on Bayer-AA and ATAB were significantly higher than that those on MPB and TAB. These higher maximum adsorption densities are consistent with requiring a smaller dose of adsorbents of Bayer-AA and ATAB to achieve the same defluoridation performance, implying a lower disposal cost for spent adsorbents. Figure 4(c) shows the amounts of spent adsorbents generated during defluoridation, indicating that the ATAB exhibits a great potential to having the lowest disposal cost for spent adsorbents. The amounts of spent adsorbents generated for the same service with Bayer-AA, MPB and TAB were about 3X, 15X, and 9X higher, respectively, than the spent adsorbent generated for the same service with ATAB. It was worth noting that the aforementioned analyses were performed based on a single use of adsorbent for defluoridation. According to the previous study,[28] the material costs of defluoridation using Bayer-AA with regeneration were approximately 50% cheaper than the single-use AA without regeneration. In summary, compared to the conventional Bayer-AA, the ATAB presents itself as the significantly greener alternative for groundwater and wastewater defluoridation due to its lower manufacturing costs, smaller waste disposal footprint, and a large potential for obtaining carbon offset revenues.

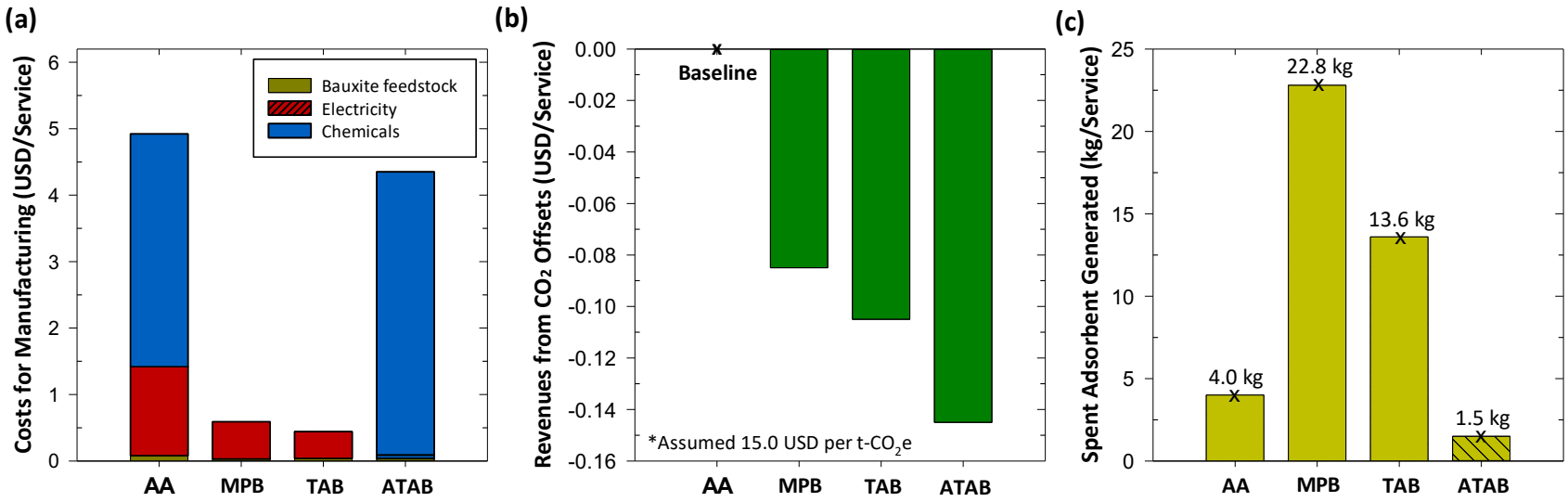

Figure 4. (a) operating costs for manufacturing of different defluoridation adsorbents. **(b)** revenues from CO_2 offsets where the carbon footprint of the Bayer-AA serves as the baseline for analysis. The average California marketplace of CO_2 offsets sold in 2018 at ~15.00 USD per tonne-CO_2e was used.[42] **(c)** the amount of spent adsorbent generated during defluoridation, potentially indicating the subsequent disposal costs associated with defluoridation. Note that all analyses are based on per service, i.e., remediating one tonne of groundwater by adsorption from an initial fluoride concentration of 10 mg/L down to a final concentration of 1.5 mg/L.

IMPLICATIONS: DEPLOYMENT OF GREENER ADSORBENTS FOR SUSTAINABLE WATER SUPPLY

Life-cycle thinking asks companies and consumers and countries to take responsibility for GHG emissions of products and processes along their entire supply chain. As the world economy becomes more complex, it is increasingly difficult to connect consumers and other downstream users to the origins of their GHG emissions. Given the important role of subnational entities, such as cities and wastewater treatment plants, in GHG abatement efforts, it would be advantageous to better link downstream users to facilities and regulators who control primary emissions.[48] The use of Bayer-AA as an adsorbent exhibited a market of over 200 million USD/yr in 2017 in global wastewater treatment, that is predicted to grow between 5–8% annually. This study reveals the potentials of manufacturing three other bauxite-derived adsorbents that can substitute for Bayer-AA avoiding its complex, high temperature and pressure processes, as well as reduce energy consumption and hazardous waste generation. The alternative approaches meet some of the desired criteria of green chemistry principles, such as resource efficiency maximization, fewer synthetic methods, and waste prevention, compared to the commercialized Bayer process for bauxite-derived AA.

According to our analysis, these alternative approaches exhibit a significantly less energy intensity (e.g., ~89% lower in the case of ATAB) during the adsorbent manufacturing, while maintaining a competitive maximum adsorption density for fluoride. The resource efficiency (the *E* factor) of adsorbent manufacturing processes is also remarkably improved by these alternative approaches, indicating that a huge quantity of

process wastes could be avoided accordingly. For instance, replacement of Bayer-AA by ATAB can reduce the *E* factor from 7.73 to 0.27. Most importantly, replacement of Bayer-AA with ATAB for wastewater treatment could reduce the operating costs of adsorbent manufacturing by 4.7 million USD per year (based on the annual demand of AA in water treatment in 2015, namely ~33,000 tonnes), while potentially lowering carbon emissions by 20X (based on the carbon footprint of AA at ~10.0 kg CO_2-eq per service) and generating additional carbon credits of 1.2 million USD per year (based on the California carbon offsets price in 2018 at 15.0 USD per tonne-CO_2e). In other words, these alternatives provide a greener and more sustainable manufacture of bauxite-derived adsorbents that can be used for defluoridation of wastewater and groundwater. Particularly, the adoption of ATAB for use industrially as an adsorbent for fluoride from wastewater represents a more carbon friendly and cost-effective approach compared to existing Bayer-AA based technologies. In future work, it would be desired to expand the scope of life-cycle carbon footprint analysis by considering other supply-chain processes, such as bauxite mining, feedstock transport, regeneration of saturated sorbents, and final waste disposal (e.g., red mud, waste acids and bases).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.

Principle unit operations in the Bayer Process of refining alumina from bauxite; System boundary and inventory data of manufacturing activated alumina from the

Bayer process (Bayer-AA); System boundary and inventory data of the MPB process; System boundary and inventory data of the TAB process; System boundary and inventory data of the ATAB process; Average prices of limestone, sodium hydroxide and hydrochloric acid; Inventory of each scenario for achieving the same service.

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Notes

The authors declare no competing financial interest.

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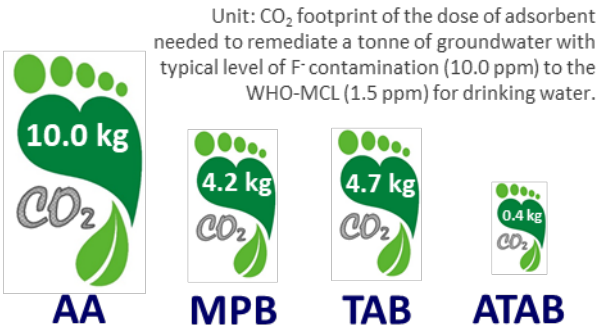

Synopsis: The adoption of ATAB for use industrially as an adsorbent for wastewater defluoridation represents a more carbon friendly approach compared to existing Bayer-AA.